

Effect of Composition and Post-Deposition Annealing on the Etch Rate of Hafnium and Zirconium Silicates in Dilute HF

J. J. Chambers, A. L. P. Rotondaro, M. J. Bevan,
M. R. Visokay, and L. Colombo
Texas Instruments Incorporated
Silicon Technology Research, Dallas, TX 75243

OBJECTIVE

As the gate dimensions of complementary-metal-oxide-semiconductor (CMOS) devices approach sub-100 nm, the thickness of the silicon dioxide dielectric pushes the gate leakage farther into direct tunneling. In this regime, tunneling current increases exponentially as the dielectric thickness decreases. Aggressively scaled devices would benefit from an alternate high dielectric constant (high-k) gate material that enables a thicker dielectric to reduce gate leakage at a given equivalent oxide thickness while also maintaining the high mobility of the silicon dioxide/silicon interface. Silicate materials are being investigated as high-k dielectrics to take advantage of the high dielectric constant of a binary metal oxide combined with the thermal stability and excellent interfacial properties of SiO₂. Although high-k dielectrics may offer some advantages over SiO₂, integration of these materials into a standard CMOS flow remains a challenge. For instance, the knock-on of metal into the source/drain regions may warrant the removal of the high-k film before ion implantation, and silicidation of the source/drain regions requires the removal of the high-k film. A wet chemistry to etch high-k dielectrics would be advantageous to avoid plasma damage during a dry etch. Therefore, the wet etch behavior of high-k dielectrics needs to be addressed.

The objective of this work is to measure the etch rate of hafnium and zirconium silicates in dilute hydrofluoric acid. The etch rates were determined as a function of composition and annealing and are compared to the etch rates of thermal SiO₂ and physical vapor deposited hafnium oxide. The etch rate of hafnium and zirconium silicates are found to decrease with increasing metal oxide mole fraction and increasing thermal budget. The selectivity of silicates to SiO₂ in dilute hydrofluoric acid ranges from 1:0.3 for an as-deposited silicate to 1:12 for a silicate subjected to a 1000 °C N₂ anneal.

APPROACH

Zirconium silicate films (~180 Å) were deposited using chemical vapor deposition (CVD), and hafnium silicate films (~100-180 Å) were deposited using both physical vapor deposition (PVD) and CVD. PVD hafnium silicate films were deposited at a nominal HfO₂:SiO₂ ratio of 50:50, and CVD hafnium silicate and zirconium silicate films were

deposited at nominal metal oxide to SiO₂ ratios of 20:80, 30:70 or 60:40. Hafnium oxide films (~40 Å) were deposited by PVD. Some films underwent a post-deposition rapid thermal anneal (RTA) in 1 atm N₂ at 1000 °C for 30s. The as-deposited and annealed films were then etched in dilute (0.49 %) HF using a spray processor. Pre- and post-etch film thickness was measured by ellipsometry using a single-layer model with a fixed refractive index of 2.1.

RESULTS

The etch rate of thermal SiO₂ in dilute HF is measured at 23 Å/min, as shown in Fig. 1. Figure 2 exhibits the dependence of the PVD hafnium silicate etch rate on thermal budget. The measured etch rate of an as-deposited PVD hafnium silicate is 85 Å/min. Similar etch rates (~70-100 Å/min) were obtained for as-deposited CVD hafnium silicate (not presented here). Subjecting the hafnium silicate to a 1000 °C anneal decreased the etch rate to 2 Å/min. The etch rate dependence on thermal budget of PVD hafnium oxide is presented in Fig. 3 (note the change in the x-axis scale). As-deposited hafnium oxide etches at a rate of 33 Å/min, however the etch rate diminished to <0.1 Å/min after a 1000 °C anneal. Figure 4 presents the effect of composition on the etch rate of CVD hafnium silicate. The etch rate of hafnium silicate was reduced from 16 to 1.2 Å/min when the hafnium silicate composition was changed from silicon-rich (30:70) to metal-rich (60:40). A similar dependence on composition is observed in the CVD zirconium silicate etch rate illustrated in Fig. 5. When the nominal ZrO₂:SiO₂ ratio was increased from 20:80 to 60:40, the etch rate of zirconium silicate dropped from 23 to 2.6 Å/min.

The results presented in Figs. 1-5 illustrate that the etch rate of silicates in dilute HF can be much greater or much less than that of thermal SiO₂ depending on the composition and the thermal history of the silicate. For example, the selectivity (1:0.3) of as-deposited PVD hafnium silicate to SiO₂ dropped sharply to 1:12 after a 1000 °C anneal. The selectivity of hafnium and zirconium silicate decreased by an order of magnitude from ~1:1 to ~1:10 when the composition was changed from silicon-rich to metal-rich. Furthermore, the etch rate of silicates can be similar to SiO₂ when the SiO₂ fraction is high, as in the case of annealed 30:70 CVD hafnium silicate and 20:80 CVD zirconium silicate where the selectivities to SiO₂ are 1:1.4 and 1:1, respectively.

The etch rate of PVD hafnium oxide exhibits a stronger dependence on thermal budget compared to PVD hafnium silicate. The selectivity of as-deposited PVD hafnium oxide changed from ~1:1 to <1:400 after a 1000 °C anneal. Comparing the etch rate of annealed PVD hafnium silicate and hafnium oxide (2 and <0.1 Å/min, respectively) reveals the

chemical inertness of hafnium oxide in dilute HF.

Low selectivity of high-k dielectrics to SiO₂ can be problematic when attempting to clear high-k films from over silicon and SiO₂ regions simultaneously. Over-etching high-k dielectrics under these conditions could lead to excessive removal of SiO₂ from the isolation regions of a device. Integration of high-k dielectrics may require new etch processes with high selectivity to SiO₂.

CONCLUSIONS

This work reports on the effects of composition and post-deposition RTA on the etch rates of hafnium and zirconium silicates in dilute HF. In general, the etch rate decreases as the silicon content decreases and the thermal budget increases. If a silicate has a high SiO₂ fraction and/or a low thermal budget, then HF may be an appropriate silicate etch solution. However, if a silicate has a low SiO₂ fraction and/or a high thermal budget, then HF may not be a suitable etch solution, since a significant amount of the isolation may be removed during silicate over-etch.

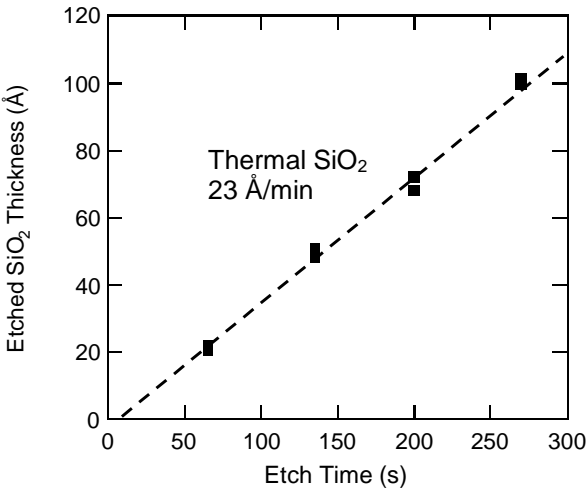


Figure 1. Etch rate of thermal SiO₂ in dilute HF.

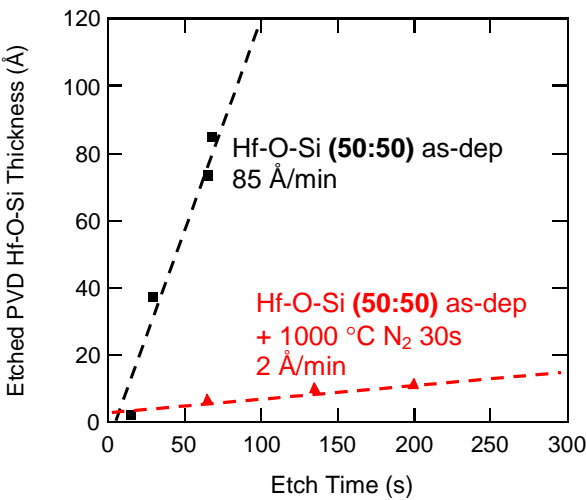


Figure 2. Effect of thermal budget on the etch rate of PVD hafnium silicate in dilute HF.

These results indicate that the composition and thermal history of hafnium and zirconium silicates must be taken into account when choosing a wet etch process, and that alternate etch chemistries may need to be developed for high-k dielectrics.

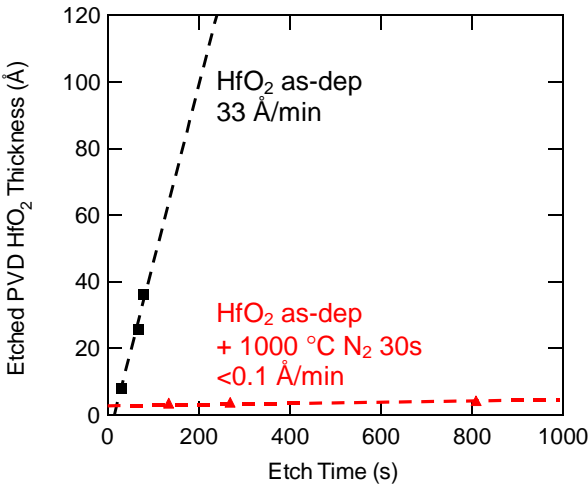


Figure 3. Effect of thermal budget on the etch rate of PVD hafnium oxide in dilute HF.

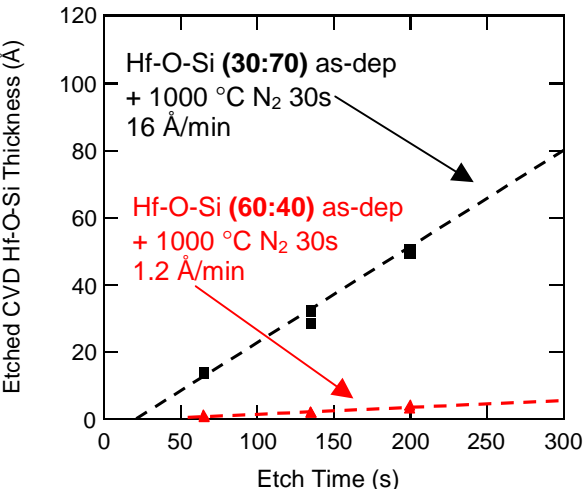


Figure 4. Effect of composition on the etch rate of CVD hafnium silicate in dilute HF.

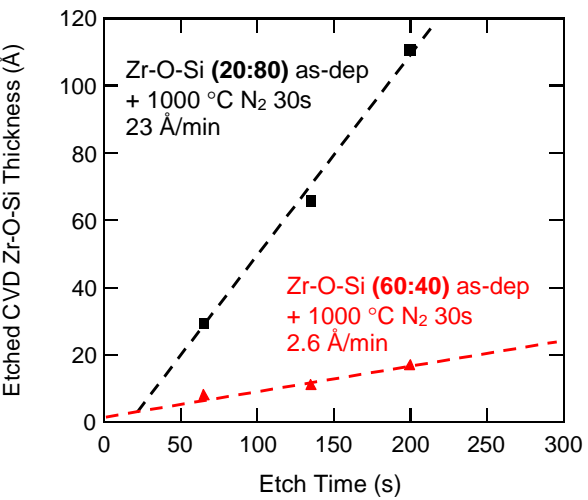


Figure 5. Effect of composition on the etch rate of CVD zirconium silicate in dilute HF.